



Synthesis and characterization of partly fluorinated poly(phthalazinone ether)s crosslinked by allyl group for passive optical waveguides

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ABSTRACT

It is necessary to introduce cross-linkable groups onto polymer chains as the processability and thermal stability of the polymers for passive waveguide device applications are very dependent on their cross-linking capabilities. Herein a series of novel cross-linkable allyl-containing fluorinated poly(phthalazinone ether)s (Allyl-FPPEs) have been prepared by a modified polycondensation of 4-(4-hydroxyphenyl)(2*H*)-phthalazin-1-one (DHPZ), decafluorobiphenyl (DFBP), 4,4'-(hexafluoroisopropylidene)diphenol (6F-BPA), and 3,3'-diallyl-4,4'-dihydroxybiphenyl (DA-DHBP) for optical waveguide applications. The obtained random polymers were characterized by FT-IR, NMR and GPC. The resulting polymers having good solubility in polar organic solvents at room temperature, can be easily spin-coated into thin films with attracting optical quality, good thermal stabilities (the temperatures of 1% mass-loss after curing: 455–503 °C), and high glass transition temperatures (T_g s: 167–251 °C) which could further increase by about 20 °C after thermal cross-linking. The crosslinked polymer films exhibit good optical properties. By adjusting the feed ratio of the reactants, the refractive indices of TE and TM modes (at 1550 nm) could be well controlled in the range of 1.4998–1.5618 and 1.4954–1.5520, respectively. The optical losses of the crosslinked polymers possess rather low values, less than 0.3 dB/cm at 1550 nm.

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1. Introduction

Polymeric materials have been considered as promising and potential candidates for constructing waveguide devices and circuits capable of performing the required functions for integrated optics [1,2]. The key requirements of the polymer optical waveguide materials include low optical loss in the infrared (IR) region, high thermal stability, good refractive index controllability, low birefringence, and good adhesion with silicon substrates. Traditional polymer materials have high optical loss in the IR communication region due to the vibrational overtones of the C–H, O–H and N–H bonds [3,4]. Fluorination and deuteration are effective methods to reduce C–H bond overtone absorption because substitution of C–F or C–D for C–H shifts the absorption band to higher wavelength as well as it makes the intensity weak. In the past twenty years, many polymers such as deuterated or fluorinated acrylates [5,6], benzocyclobutenes [7], perfluorocyclobutanes [8],

fluorinated dendrimers and hyperbranched polymers [9,10], fluorinated polyimides [11–15], deuterated polyfluoromethacrylates [16], polysiloxanes and inorganic–organic hybrid polymers [17,18], polycarbonates [19–21], and fluorinated poly(arylene ether)s [22–28], have been synthesized for optical passive waveguide application. Among them, fluorinated poly(arylene ether)s are proved to be one of classes of promising candidates due to their low intrinsic absorption at telecommunication wavelengths, good thermal, mechanical and chemical stability [22–28]. In our previous study, we synthesized a series fluorinated poly(arylene ether)s (FPPEs) containing phthalazinone moieties derived from 4-(4-hydroxyphenyl)(2*H*)-phthalazin-1-one (DHPZ), decafluorobiphenyl (DFBP) and 4,4'-(hexafluoroisopropylidene)diphenol (6F-BPA) by modified nucleophilic polycondensation at lower reaction temperature to suppress the side reaction due to the high reactivity of *ortho*-fluorine of DFBP [27]. FPPEs with the fluorine content of 28.57–42.09 wt% per repeating unit exhibited good optical transparency (less than 0.27 dB/cm at 1310 nm) and high glass transition temperatures (T_g s: 185–269 °C) compared to the fluorinated poly(arylene ether)s with 27.48–41.37 wt% fluorine content per repeating unit reported [23]. However, the birefringences of these FPPEs we reported were still higher than that expected for

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non-polarization passive optical waveguide devices. It is reported that crosslinked polymers have several advantages such as increased thermal stability, good chemical resistance, and improved adhesion properties at the substrate. Moreover, introducing cross-linkable groups into polymer backbones is also essential for the multi-layer fabrication of a waveguide device. Generally there are several ways to introduce cross-linkable group onto polymer backbone, for instance, (A) as pendent groups, (B) as internal groups, (C) in the polymer chains. In optical polymer waveguide materials bearing terminal ethynyl or phenylethynyl groups initially reported [22,23], as the cross-linking reaction occurs only at the polymer chain ends, the theoretical cross-linking density of the cured polymer is limited. Recently research interests focus on introducing cross-linkable groups into polymer chains as internal groups or in the polymer chains [24–26,28]. In addition, it is essential that polymer optical materials should have tunable refractive index, since selecting the same kind of polymers to fabricate both the core and the cladding layers is of advantage to a good interface adhesion and comparable thermal expansion coefficients between the two layers. Herein we designed and synthesized a series of novel cross-linkable fluorinated poly(phthalazinone ether)s (Allyl-FPPEs) with tunable refractive index by introducing allyl moiety into the polymer main chain to improve the multi-layer processability, while maintaining the other attracting properties, such as still acceptable optical loss in 1550 nm, low birefringence, and high thermal stability.

2. Experimental

2.1. Materials

3,3'-Diallyl-4,4'-dihydroxybiphenyl was synthesized according to the procedure reported previously [29]. The product was obtained as white crystal, m.p.: 82–83 °C, and confirmed by ^1H NMR (400 MHz, CDCl_3 , ppm) δ : 3.46 (m, 4H), 4.93 (s, 2H), 5.15–5.23 (m, 4H), 6.00–6.10 (m, 2H), 6.85 (d, 2H, 8 Hz), 7.25–7.32 (m, 4H). *N,N'*-dimethylacetamide (DMAc) was vacuum-distilled over calcium hydride and stored over molecular sieves (type 4 Å) before used. 4-(4-Hydroxyphenyl)(2H)-phthalazin-1-one (DHPZ) was gifted by Dalian Polymer New Materials Co. Ltd., PR China. Decafluorobiphenyl (DFBP) and 4,4'-(hexafluoroisopropylidene)diphenol (6F-BPA) were purchased from Aldrich Chemical Co. and used as received. Analytical-grade anhydrous potassium fluoride (KF), calcium hydride (CaH_2), tetrahydrofuran (THF), chloroform (CHCl_3), *N*-methyl pyrrolidone (NMP) and cyclohexanone were purchased from Tianjin Fuyu Fine Chemical Industry Co., Ltd., PR China, and used without any further treatment.

2.2. Instruments

^1H NMR (400 MHz) and ^{19}F NMR (376 MHz) spectra were obtained with a Varian Unity Inova 400 spectrometer at an operating temperature of 25 °C using CDCl_3 as a solvent and were listed in parts per million downfield from tetramethylsilane (TMS), respectively. Fourier transform infrared (FT-IR) spectra were recorded by reflection method with a Thermo Nicolet Nexus 470 Fourier transform infrared spectrometer. Gel permeation chromatography (GPC) analysis was carried out on a HP 1090 HPLC instrument equipped with 5 μm Phenogel columns (linear, 4500 Å) arranged in series with chloroform as eluent and a UV detector at 254 nm. And the values were calibrated versus polystyrene standard. The glass transition temperature (T_g) was determined with a Mettler DSC 822 differential scanning calorimetry (DSC) in flowing nitrogen at a heating rate of 10 °C min^{-1} from 50 to 350 °C. Thermogravimetric analysis (TGA) of the polymer was performed on a Mettler TGA/SDTA851 thermogravimetric analysis instrument in a nitrogen atmosphere at a heating rate of 20 °C min^{-1} from 100 to 700 °C.

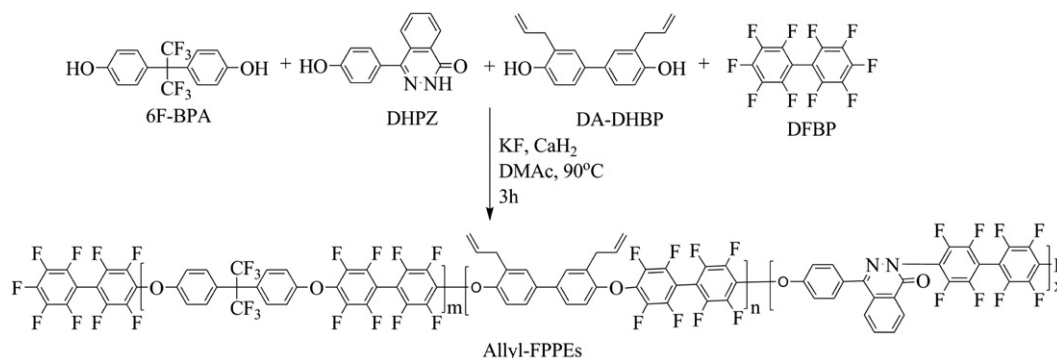
The gel content of the crosslinked samples was determined according to ASTM D2765 method. Samples were extracted by Soxhlet's apparatus in cyclohexanone for 48 h. The residue after extraction was taken as the gel component, and the gel content was calculated according to the following equation (1).

$$\text{Gel content} = \frac{W_2}{W_1} \times 100\% \quad (1)$$

where W_1 and W_2 are the weights of the samples before and after refluxed in cyclohexanone for 48 h.

2.3. Polymer synthesis

A typical synthetic procedure of Allyl-FPPE-3 was described as follows (shown in Scheme 1). A mixture of 6F-BPA (1.5130 g, 4.5 mmol), DHPZ (1.0721 g, 4.5 mmol), DFBP (3.4080 g, 10.2 mmol), DA-DHBP (0.2663 g, 1 mmol), anhydrous KF (0.1162 g, 2 mmol) and CaH_2 (0.8419 g, 20 mmol) and 30 mL DMAc was placed in a 100 mL three-necked round-bottomed flask equipped with a mechanical stirrer, a nitrogen inlet and outlet. The reaction mixture was constantly stirred and heated to 90 °C for 3 h. Then the solution was slowly poured into sufficient ethanol at the presence of hydrochloric acid in drops. The crude polymer was rinsed six times with hot distilled water to remove inorganic salts. The dried polymer was purified by dissolving in DMAc, being filtered through a 0.45 μm Teflon microfilter before pouring into ethanol, and subsequently rinsed six times with hot deionized water.



Scheme 1. Synthesis of Allyl-FPPEs.

The purified polymer was dried at 120 °C under vacuum for 24 h. The products were obtained in yield 92 wt%. Selected data of Allyl-FPPE-3: ^1H NMR (40 MHz, CDCl_3 , ppm) δ : 3.65 (d, 5.6 Hz), 5.16 (m), 6.10 (m), 6.81 (d, 8.0 Hz), 7.06 (d, 8.0 Hz), 7.24 (d, 8.0 Hz), 7.42 (d, 8.0 Hz), 7.68 (d, 8.0 Hz), 7.8–8.00 (m), 8.63 (s); ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ : –64.06 (s), –136.63 (m), –137.46 (m), –138.02 (m), –143.30 (m), –152.40 (m), –153.16 (m).

Allyl-FPPEs with different fluorine contents were prepared using the similar procedures as outlined above and characterized as follows.

Allyl-FPPE-1: ^1H NMR (400 MHz, CDCl_3 , ppm) δ : 3.65 (d, 5.6 Hz), 5.16 (m), 6.10 (m), 7.42 (d, 8.0 Hz), 6.81 (d, 8.0 Hz), 7.68 (d, 8.0 Hz), 7.80–8.00 (m), 8.63 (s). ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ : –136.64 (m), –137.50 (m), –138.01 (m), –143.27 (m), –152.45 (m), –153.16 (m).

Allyl-FPPE-2: ^1H NMR (400 MHz, CDCl_3 , ppm) δ : 3.65 (d, 5.6 Hz), 5.16 (m), 6.10 (m), 6.81 (d, 8.0 Hz), 7.06 (d, 8.0 Hz), 7.24 (d, 7.6 Hz), 7.42 (d, 8.0 Hz), 7.68 (d, 8.0 Hz), 7.80–8.00 (m), 8.63 (s). ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ : –64.05 (s), –136.65 (m), –137.51 (m), –138.01 (m), –143.28 (m), –152.45 (m), –153.16 (m).

Allyl-FPPE-4: ^1H NMR (400 MHz, CDCl_3 , ppm) δ : 3.65 (d, 5.6 Hz), 5.16 (m), 6.10 (m), 6.81 (d, 8.0 Hz), 7.06 (d, 8.0 Hz), 7.24 (d, 7.6 Hz), 7.42 (d, 8.0 Hz), 7.68 (d, 8.0 Hz), 7.80–8.00 (m), 8.63 (s). ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ : –64.06 (s), –136.65 (m), –137.48 (m), –138.03 (m), –143.30 (m), –152.38 (m), –153.17 (m).

Allyl-FPPE-5: ^1H NMR (400 MHz, CDCl_3 , ppm) δ : 3.65 (d, 5.6 Hz), 5.16 (m), 6.10 (m), 6.81 (d, 8.0 Hz), 7.06 (d, 8.0 Hz), 7.24 (d, 7.6 Hz), 7.42 (d, 8.0 Hz). ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ : –64.07 (s), –137.47 (m), –138.04 (m), –152.39 (m), –153.18 (m).

2.4. Thermal-curing properties of Allyl-FPPEs

Allyl-FPPEs were firstly dissolved in chloroform at a concentration of 30 wt%. Then the films were cast from the solution and dried at room temperature under vacuum. The thermal cross-linking processes of the films were then performed by heating the polymer films at 280 °C for 2 h under vacuum. The effect of thermal cross-linking on T_g was detected by DSC.

2.5. Film preparation and optical properties measurements

The substrates used in the experiments were highly polished Si/ SiO_2 wafers. Organic residues on the silicon surfaces were removed by the successive ultrasonic cleaning with acetone, alcohol and then ion free pure water, sequentially. The polymer solutions were prepared by dissolving the obtained polymers (20 wt%) in cyclohexanone. Then the solutions were filtered through a 0.22 μm Teflon microfilter and spin-coated on a Si/ SiO_2 wafer substrates at a spin rate of 500 rpm for 10 s, followed by 1000–4000 rpm for 30 s. The resulting films were dried at 60 °C for 30 min to remove the residual solvent under high vacuum. Thermal cross-linking was then performed by heating the films slowly to 280 °C and

maintaining at this temperature for 2 h. The refractive indices of the polymer films were measured by the prism-coupling method at the wavelengths of 1550 nm with the tolerance of ± 0.0002 . The optical losses of the polymer films were measured on slab waveguide samples using the high-index liquid immersion technique. In this technique, light was coupled to a slab waveguide by prism-coupling. After propagating for a certain distance, the light was out-coupled from the waveguide by immersing it into a high-index liquid. And the propagation loss could be calculated with the out-coupled optical power described as a function of the propagation distance. Optical properties such as refractive index and optical loss were measured by using a Sairon SPA-4000 prism coupler with the tolerance of ± 0.0002 .

3. Results and discussion

3.1. Synthesis of Allyl-FPPEs

Traditionally, the synthesis of poly(arylene ether)s is carried out at high temperatures, such as higher than 150 °C, in polar aprotic solvents, such as dimethylsulfoxide and sulfolane, in the presence of potassium carbonate as the base. In these conditions, there exist side cross-linking reactions in the polycondensation reaction of bisphenols and perfluorinated monomers, such as decafluorobiphenyl, because of the high reactivity of other fluorine atoms except the *para*-position fluorine atom. Allyl group of 3,3'-diallyl-4,4'-dihydroxybiphenyl was also rearranged into propenyl group in these reaction conditions because the potassium carbonate in the reaction mixture acted as the base-catalyst to isomerize allyl group to propenyl group [29–31]. Ding et al. reported a modified polycondensation procedure suitable for preparing high fluorinated poly(arylene ether)s. Their polymerization system occurred at lower reaction temperature by using suspending CaH_2 with trace amount of KF, instead of potassium carbonate, as catalyst [32]. Under this procedure, 3,3'-diallyl-4,4'-dihydroxybiphenyl was stable during the reaction. Therefore, we explored our polymerization reaction using this approach. The stoichiometric phthalazine-containing bisphenol-like monomer DHPZ, fluorinated monomer 6F-BPA, allyl-containing bisphenol, DA-DHBP, and activated dihalogenated compound decafluorobiphenyl (DFBP) reacted in the reactive medium at 90 °C which was experimentally optimized. Herein the feed ratio of DA-DHBP was brought into a constant of 10 mol% (relative to the total bisphenols) to enable the formation of cross-linking networks, and the feed ratio of 6F-BPA was varied from 0 to 90 mol% on the basis of the total bisphenol monomers to tune the refractive index. After the reaction underwent at 90 °C for 3 h, GPC analysis of the resulting polymers revealed that they had averaged number molecular weights over 20,000 and polydispersities in the range of 2.2–2.8 (Table 1), respectively.

The resulting polymers exhibited good solubility in polar organic solvents such as THF, CHCl_3 , cyclohexanone, DMAc, DMF,

Table 1
Results of polymerization.

Polymers	6F-BPA content ^a (mol%)	DHPZ content ^b (mol%)	DHPZ content from ^1H NMR ^c	M_n^d ($\times 10^4$)	M_w^d ($\times 10^4$)	n^e
Allyl-FPPE-1	0	90	89.6	2.59	7.31	2.81
Allyl-FPPE-2	22.5	67.5	67.2	2.37	6.18	2.64
Allyl-FPPE-3	45	45	43.7	2.31	5.54	2.40
Allyl-FPPE-4	67.5	22.5	22.6	2.51	6.41	2.56
Allyl-FPPE-5	90	0	0	2.07	4.62	2.22

^a Feed molar ratio of 6F-BPA relative to the total bisphenols.

^b Feed molar ratio of DHPZ relative to the total bisphenols.

^c Feed molar ratio of DHPZ relative to the total bisphenols.

^d M_n , M_w values were determined by GPC in CHCl_3 with PS as standard.

^e n values (M_w/M_n) were determined by GPC in CHCl_3 with PS as standard.

Table 2

The solubility of the Allyl-FPPEs.

Polymers	CHCl ₃	THF	Acetone	DMSO	NMP	DMAc	Benzene	DMF	Py
Allyl-FPPE-1	+	+	+	–	+	+	+	+	+
Allyl-FPPE-2	+	+	+	–	+	+	+	+	+
Allyl-FPPE-3	+	+	+	–	+	+	+	+	+
Allyl-FPPE-4	+	+	+	–	+	+	+	+	+
Allyl-FPPE-5	+	+	+	–	+	+	+	+	+

“+”: soluble in room temperature; “–”: insoluble.

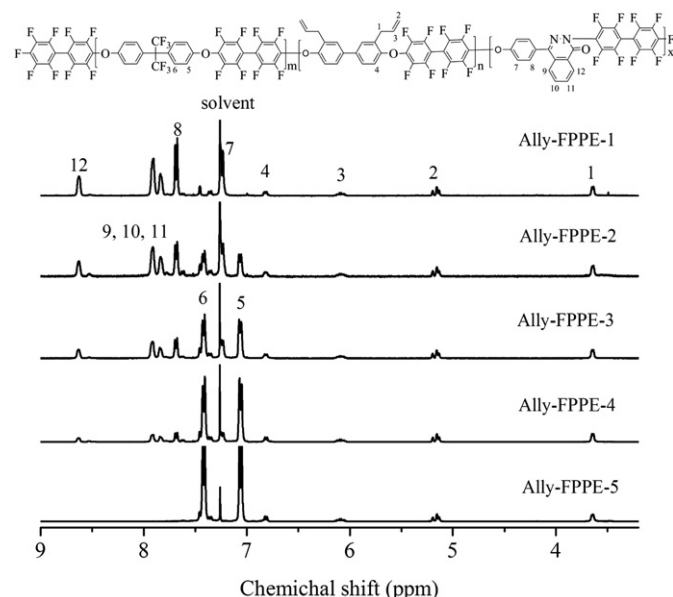
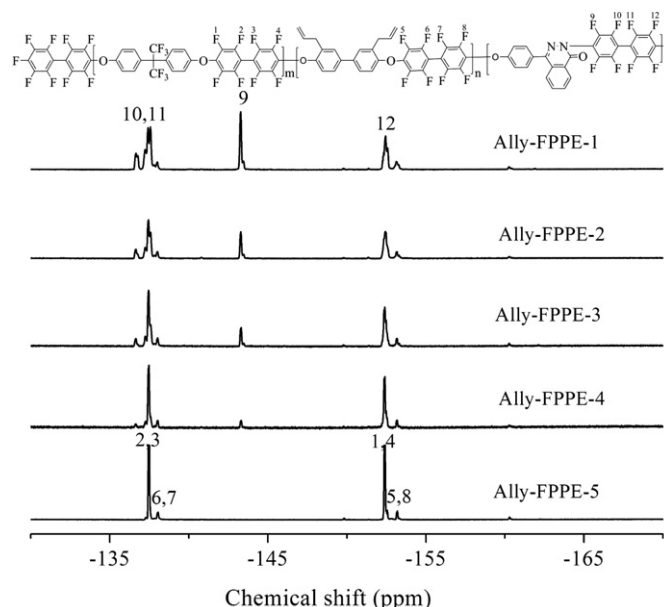
NMP at room temperature (see Table 2). The solution of the polymers in the above solvents can easily filtrated through 0.22 μm Teflon microfilter illustrating that the obtained polymer had no microgel formed indicative of linear polymers.

3.2. Characterizations and properties of polymers

The obtained polymers were characterized by ¹H NMR, ¹⁹F NMR, and FT-IR. The ¹H and ¹⁹F NMR spectra of Allyl-FPPEs are shown in Figs. 1 and 2, respectively.

On detailed examination of the ¹H NMR spectra, it was observed that all pictures of the copolymers exhibited the signals of four hydro protons at 3.65, 5.16, and 6.10 ppm attributed to the allyl group of the DA-DHBP units. These peaks showed almost same integration for all the copolymers. The polymers except Allyl-FPPE-5 had the typical signal of phthalazinone segment around 8.6 ppm which increased with the increasing feed ratio of DHPZ. The aromatic peaks at 7.5–8.0 ppm and around 7.24 ppm were due to the phthalazinone units and the peaks around at 7.06 and 7.42 ppm are ascribed to the 6F-BPA units. Some small peaks at 7.35 and 7.62 ppm were attributed to the DA-DHBP units.

Their ¹⁹F NMR spectra, as shown in Fig. 2, further confirmed the structure of the resulting polymers. Two little peaks around at –138.0 and –153.0 ppm were attributed to F6, 7 and F5, 8 which belonged to the allyl-containing segment, respectively. The intensities of two peaks at –137.5 and –152.4 ppm owing to the F2, 3 and F1, 4 of the bisphenol 6F-BPA, respectively, decreased proportionally with the decrease of the feed ratio of 6F-BPA. In an asymmetric monomer DHPZ, the peak F9 adjacent to –N– of lactam and the peak F12 adjacent to –O– appeared at –143 and –152.5 ppm,

**Fig. 1.** ¹H NMR spectra of Allyl-FPPEs.**Fig. 2.** ¹⁹F NMR spectra of Allyl-FPPEs.

respectively. No obvious signal related to branching of the polymer chains was observed from the ¹⁹F NMR spectra.

Additionally, all of the FT-IR of Allyl-FPPEs showed the characteristic absorption bands near 1690 cm^{–1} (C=O stretching), 1605 cm^{–1}, 1488 cm^{–1} (C=C stretching vibration of the aromatic ring), 1260 cm^{–1} and 1210 cm^{–1} (Ar–O–Ar stretching). These characteristic bands in IR spectra were correlated sufficiently well with the expected structure of the target substance.

3.3. Thermal cross-linking of the polymers

The *T*_gs of our polymers were measured by DSC at heating rate of 10 °C/min under nitrogen atmosphere, and the results are summarized in Table 3. Their DSC heating scans exhibited only one distinct *T*_g in the range of 167–251 °C. According to Fox equation, the *T*_g of a random copolymer can be predicted based on the feed ratio of the monomers as presented in Fig. 4 using equation (2):

$$\frac{1}{T_g} = \frac{Wt_1}{T_{g1}} + \frac{Wt_2}{T_{g2}} \quad (2)$$

where *T*_g is the glass transition temperature of the copolymer, *Wt*₁ is the sum of the weight fractions of the repeat units which contain DHPZ relative to the all repeat units, *Wt*₂ is the sum of the weight fractions of the repeat units which contain 6F-BPA or DA-DHBP relative to the all repeat units, *T*_{g1}, and *T*_{g2} are the glass transition temperatures of the ‘homopolymers’ derived from DHPZ with DFBP (*T*_{g1} = 269 °C) [27] and from DA-DHBP and 6F-BPA with DFBP (*T*_{g2} = 167 °C), respectively. Fig. 4 displayed the measured *T*_g and the predicted trend line according to the Fox equation. A good agreement of the *T*_gs of the resulting copolymers with the values predicted by the Fox equation was observed. Thus, it can be concluded that the three bisphenol comonomers, i.e., 6F-BPA, DA-DHBP and DHPZ, have been randomly incorporated into the polymers. The random chain structure of the polymers ensures a homogeneous morphological structure with minimized fluctuations of density and refractive index in the film [25], so that the optical loss aroused from light scattering was minimized.

Table 3
Optical and thermal properties of Allyl-FPPEs.

Polymers ^a	n_{TE} ^b	n_{TM} ^b	Δn ^c	Optical loss ^d (dB/cm)	Gel content ^e (%)	T_g^f (°C)	T_g^g (°C)	$T_{1\%d}^h$ (°C)
Allyl-FPPE-1	1.5618	1.5520	0.0098	0.297	86.7	251	276	503
Allyl-FPPE-2	1.5448	1.5374	0.0074	–	88.3	238	261	498
Allyl-FPPE-3	1.5279	1.5222	0.0057	0.288	90.2	209	227	492
Allyl-FPPE-4	1.5127	1.5078	0.0049	–	89.5	193	200	458
Allyl-FPPE-5	1.4998	1.4954	0.0044	0.277	87.4	167	180	455

^a The sample codes were the same as shown in Table 1.

^b Refractive index of the TE mode or TM mode at 1550 nm.

^c $\Delta n = n_{TE} - n_{TM}$.

^d Measured on slab waveguide samples using the high-index liquid immersion technique at 1550 nm.

^e Gel content for cured samples.

^f Glass transition temperature measured by DSC with a heating rate of 10 °C/min in nitrogen before cured.

^g Glass transition temperature measured by DSC with a heating rate of 10 °C/min in nitrogen in the second scan.

^h Thermal decomposition temperature, defined as the temperature of 1% weight loss, at a heating rate of 20 °C min^{−1} in nitrogen after curing.

The allyl unity in the copolymers can undergo addition reaction by thermal heating without any initiator. Thus the thermal cross-linking reaction of Allyl-FPPEs was investigated by heating the polymer films at 280 °C for 2 h in vacuum in the absence of any initiator. The characteristic absorption of the vinyl group near 917 cm^{−1} out of plane vibrations of the vinyl group, CH₂=CH was selected to monitor the reaction by FT-IR spectroscopy. Fig. 3 exhibited the comparisons of FT-IR spectra of Allyl-FPPE-1 film before and after curing. The absorption peak near 917 cm^{−1} disappeared totally after curing. Two methods were experimentally used to detect the extent of the cross-linking reaction. Firstly, the polymer films were also soaked in cyclohexanone for 24 h at room temperature, and then dried for 24 h at 120 °C under vacuum. It was found that the resulting films exhibited less change of their weight. The cured films were also extracted in cyclohexanone by using Soxhlet's apparatus. And then the gel contents of the polymers were calculated according to equation (1). The result was indicated that the gel contents of the copolymers were all more than 86% suitable for multi-layer process. The T_g s of all the polymers, except Allyl-FPPE-4, was increased almost about 20 °C after curing, as Table 3 shown.

The thermal stability of curing polymers was investigated by thermogravimetric analysis (TGA) at heating rate of 20 °C/min under nitrogen atmosphere. Their onset temperatures of 1% weight loss were over 455 °C. Especially, with the increase of

phthalazinone moieties in the polymer chain, such as more than 45%, this value was almost near to 500 °C, indicating the excellent thermal stability of our polymers.

3.4. Film preparation and optical properties of Allyl-FPPEs

The refractive indices of TE and TM mode, n_{TE} and n_{TM} , of the crosslinked polymer thin films were determined using the prism-coupling technique at the 1550 nm wavelength, listed in Table 3. The refractive index could be controlled exactly by adjusting the 6F-BPA content from 0 to 90 mol% (relative to the total bisphenols), as shown in Fig. 5. With the decrease of the 6F-BPA content, the refractive indices of TE and TM modes increase from 1.5618 to 1.4998 and from 1.5520 to 1.4954, respectively. Since the refractive index could change with the free volume (packing density), polarizability of the material, temperature, and humidity [23], it seems to easily explain that the decrease of refractive indices is attributed to the smaller electronic polarizability and large free volume of the C–F compared to C–H bond. The controllability of refractive index enables for the use of the materials for core and cladding layers of various optical waveguide devices.

The birefringence is related to the optical anisotropy of the polymer material [23] which stems mainly from the preferred orientation of rigid groups and polymer chains. Meanwhile, the existence of crank and twisted non-coplanar phthalazinone moiety

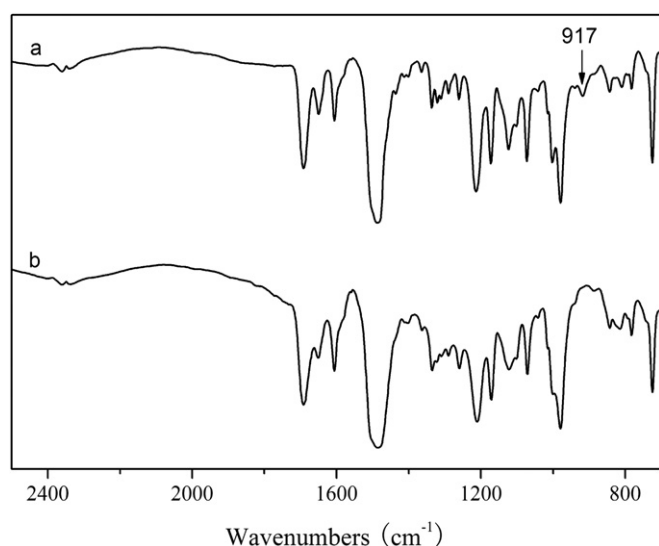


Fig. 3. FT-IR spectra of Allyl-FPPE-1 (a) before curing (b) after curing at 280 °C for 2 h under vacuum.

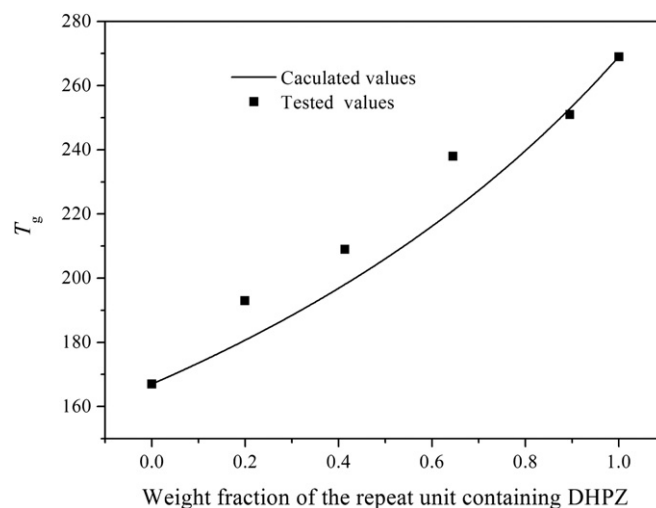


Fig. 4. Correlation between T_g of Allyl-FPPEs and the weight fraction of the repeat unit containing DHPZ: (■) experimentally determined T_g values from DSC. The solid line represents the calculated values according to the Fox equation.

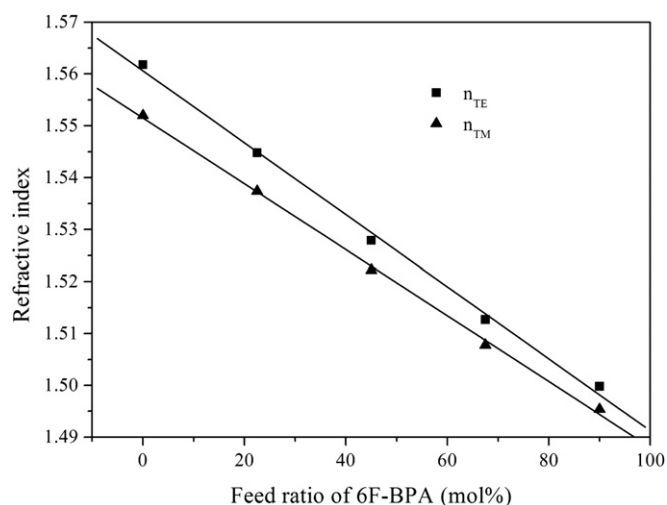


Fig. 5. Dependence between refractive index and 6F-BPA content (mol%) at 1550 nm.

into the main chain may reduce the regularity of the main chain, cumber the close packing of chains and hinder the movement of the main chain. Compared to the 6F-BPA units in the polymer chains, the phthalazinone structure of DHPZ has more rigid units which can lead large birefringence of the polymers. From Table 2, it is observed that the birefringences of the Allyl-FPPEs increased from 0.0044 to 0.0098 with increasing DHPZ content from 0 to 90 mol%. All the birefringences of our polymers were still acceptable for non-polarization device.

The optical losses of the obtained polymers were measured at 1550 nm by the high-index liquid immersion technique. The values were found to be in the range of 0.277–0.298 dB/cm, indicating relatively low optical loss of these polymers at the telecommunication wavelengths.

4. Conclusions

A series of cross-linkable fluorinated poly(phthalazinone ether)s containing cross-linkable allyl groups have been successfully synthesized by nucleophilic displacement polycondensation reaction starting from DHPZ, DFBP, DA-DHBP and 6F-BPA in the presence of KF with CaH_2 at 90 °C for 3 h. The addition reaction of the allyl groups in the polymer improved the endurance of the polymer films in multi-layers fabrication process. By adjusting the feed ratio

of the reactants, the refractive indices could be finely controlled over a wide range from 1.50 to 1.55. The optical losses of the Allyl-FPPEs exhibited less than 0.3 dB/cm at 1550 nm. These attracting properties make our Allyl-FPPEs potential optical matrixes for constructing waveguide devices. The next work of the application for fabricating the passive optical waveguide is under way in our group.

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